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B. T. GALLOWAY, *Chief of Bureau.*

THE UTILIZATION OF WASTE RAISIN SEEDS.

BY

FRANK RABAK,

*Chemical Biologist, Drug-Plant, Poisonous-Plant, Physiological,
and Fermentation Investigations.*



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Chief of Bureau, BEVERLY T. GALLOWAY.

Assistant Chief of Bureau, WILLIAM A. TAYLOR.

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DRUG-PLANT, POISONOUS-PLANT, PHYSIOLOGICAL, AND FERMENTATION INVESTIGATIONS.

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276

2

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LETTER OF TRANSMITTAL

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF PLANT INDUSTRY,
OFFICE OF THE CHIEF,
Washington, D. C., November 18, 1912.

SIR: I have the honor to transmit herewith and to recommend for publication as Bulletin No. 276 of the series of this Bureau the accompanying manuscript entitled "The Utilization of Waste Raisin Seeds," by Mr. Frank Rabak, Chemical Biologist, submitted by Dr. R. H. True, Physiologist in Charge of the Office of Drug-Plant, Poisonous-Plant, Physiological, and Fermentation Investigations.

This investigation deals with the utilization of a by-product of an agricultural industry which has hitherto been disregarded. It has been shown that the seeds removed from raisins yield technically useful products, which by their value fully justify the expense involved in separating them. It is believed that this situation is typical of many so-called agricultural waste products which are at present not fully utilized.

Respectfully,

B. T. GALLOWAY,
Chief of Bureau.

Hon. JAMES WILSON,
Secretary of Agriculture.

CONTENTS.

	Page.
Introduction.....	7
Accumulation and present disposal of raisin seeds.....	7
Examination of raisin seeds for commercial products.....	10
Sirup.....	12
Preparation.....	12
Physical properties.....	12
Chemical examination.....	12
Sugars.....	12
Acids.....	13
Production of alcohol.....	13
Commercial uses.....	13
Available quantity and value.....	14
Fixed oil.....	14
Extraction and physical properties.....	14
Chemical examination.....	14
Free acids.....	14
Saponification value.....	15
Iodin absorption.....	15
Volatile acids.....	15
Soluble acids.....	16
Insoluble acids.....	16
Acetyl value.....	16
Unaponifiable matter.....	17
Detailed examination of the insoluble acids.....	17
Mixed acids.....	18
Separation of the solid and liquid acids.....	18
Solid acids.....	19
Liquid acids.....	21
Drying property of raisin-seed oil.....	23
Comparison of raisin-seed oil with other drying oils.....	25
Raisin-seed oil as a paint and varnish oil.....	28
Raisin-seed oil as a soap-making oil.....	29
Available quantity and value.....	30
Tannin.....	30
Extraction.....	30
Analysis.....	30
Dyestuff.....	31
Use of the extract in tanning.....	32
Available quantity and value.....	33
Meal.....	33
Value as stock food.....	33
Available quantity and value.....	35
Summary.....	35

ILLUSTRATIONS.

	Page.
FIG. 1. Waste raisin seeds.....	8
2. Raisin seeding machine in operation.....	10
3. Commercial products from waste raisin seeds.....	11

THE UTILIZATION OF WASTE RAISIN SEEDS.

INTRODUCTION.

In the canning and packing operations of the fruit industry in the United States certain by-products almost invariably result, many of which, because of lack of utilization, become in the true sense waste products. In the commercial canning and drying of peaches, apricots, and prunes the pits were formerly to a large extent waste material. Through an investigation recently made in the Bureau of Plant Industry,¹ however, valuable uses were discovered for this material, and as a consequence it is now used in the manufacture of many important commercial products. In the raisin-seeding industry, which within recent years has grown to such proportions in the grape-producing sections of California, vast quantities of seed accumulate annually (fig. 1). Thus far this material has been practically wasted, and it was with the object in view of preparing products of commercial value from these waste raisin seeds that the investigation herein described was undertaken.

ACCUMULATION AND PRESENT DISPOSAL OF RAISIN SEEDS.

Some idea may be gained of the vast accumulation of raisin seeds when it is considered that 30,000 to 40,000 tons of raisins are seeded annually. By actual test it has been found that 9.75 or approximately 10 per cent of the fruit consists of seeds. There should therefore be in the neighborhood of 3,000 to 4,000 tons of this material available each year. Within the past few years the matter of utilizing waste raisin seeds has been receiving some attention from the producers, but thus far with little success. From the information at hand it appears that a brandy has been made by fermenting the sugary matter which adheres to the seeds. A high-proof alcohol has also been distilled after the fermentation. It has been reported that some fixed oil has been obtained, but whether or not this has proved successful is not definitely known.

In this connection it seems desirable to mention also the possible utilization of grape seeds, of which there is a large accumulation from the residues of wineries and grape-juice factories in this country.

¹ Rabak, F. Peach, apricot, and prune kernels as by-products of the fruit industry of the United States. Bulletin 133, Bureau of Plant Industry, U. S. Dept. of Agriculture. 1908.

The utilization of these seeds has received considerable attention in the past from foreign wine growers, but with only a limited degree of success. This may be due to the fact that only one constituent, namely, the fixed oil, seemed to be made use of. In 1827 Fontenele¹ stated that it had long been known that grape seeds contain a fixed oil, but that in France there was lack of knowledge with regard to its extraction. For several years prior to this time the oil had been used in Italy to a certain extent for illuminating purposes, rivaling olive oil from the standpoint of light, clear flame, and lack of odor. This was brought to the attention of agriculturists for the reason that the

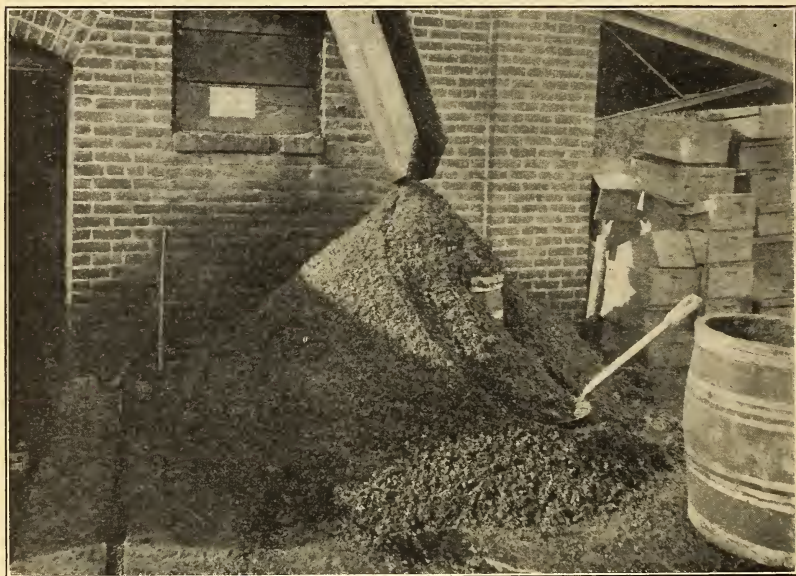


FIG. 1.—Waste raisin seeds.

seeds were being lost to them. According to Fontenele 60 pounds of the seeds produced 6 pounds of oil.

In 1828 Schübler² stated that for a long time the seeds of grapes had been utilized in the southern regions of Europe for their oil, which was used as an edible oil. It was said that the oil possessed illuminating properties, burning slowly in common lamps, being similar in this respect to poppy-seed oil, tobacco-seed oil, and the slow-burning rapeseed oil. The following year it was reported that the oil had been produced in a small way in Wurttemberg, but with no great

¹ Fontenele, J. Sur l'extraction de l'huile des pépins de raisins. *Journal de Chimie Médicale*, vol. 3, 1827, p. 66.

² Schübler, G. Untersuchungen über die fetten Oele Deutschlands in Beziehung auf ihre wichtigeren physischen Eigenschaften, 18. Oel der Weintraubenkerne, von *Vitis vinifera* L. *Journal für Technische und Ökonomische Chemie*, vol. 2, 1828, p. 364.

success.¹ In Wurttemberg alone at that time it was calculated that 340,000 pounds of grape seeds were lost annually.

According to Minutoli² the oil was said to be useful for soap-making purposes and when used in salad it was not without a pleasant taste.

The method employed for extracting the fixed oil consisted in separating the husks and stems from the seeds by drying and passing them through sieves.³ The dried seeds were ground to a meal, placed in a copper kettle, and one-third or one-fourth their weight of water added. Heat was applied and the mass was stirred continually to prevent the formation of lumps. When free fixed oil appeared upon pressure between the fingers, the mass was put into canvas bags and placed in an oil press. The cake was again treated in a similar manner and another quantity of oil produced. In this way from 10 to 20 per cent of oil was obtained from the seeds.

Marre⁴ has recently called attention to the need of reviving this industry and states that in France in the Departments of Gard, Hérault, Aude, and the Pyrénées-Orientales there are at least 28,000,000 hundredweight of grapes, or about 1,036,000 hundredweight of seeds, from which, provided a yield of 15 per cent of oil were obtained, there would result 155,000 hundredweight of oil, valued roughly at 11,655,000 francs.

According to Paris,⁵ wine residues consist of 25 to 30 per cent of stems, 50 to 60 per cent of skins, and 15 to 20 per cent of seeds, the total residue comprising about 15 to 25 per cent of the grapes. After extracting the oil the seeds contain 10.6 per cent of moisture, 9.12 per cent of crude protein, 4.2 per cent of crude fat, 45.2 per cent of crude fiber, 3.15 per cent of ash, and 27.6 per cent of nitrogen-free extractive matter, of which 11.5 per cent are carbohydrates and 12.4 per cent pentosans. The digestibility of the protein amounts to 70 per cent, fat 75 per cent, nitrogen-free extractive matter 85 per cent, and crude fiber 50 per cent. It is stated that the ash consists of 14.3 per cent of phosphorus pentoxid and 22.3 per cent of potassium oxid.

It has but recently been reported⁶ that grape-seed oil is an important product of the wine regions of France and Italy, where it is used as an edible oil and in the manufacture of soap. It is stated that 3 pounds of the oil will make 5 pounds of soap of good quality. The oil is extracted by hot or cold pressure or by solvents. On account of its high protein content the meal is said to be eaten by cattle with relish.

¹ Schübler, G. Darstellung des fetten Oels aus dem Kernen der Weintrauben. *Journal für Technische und Ökonomische Chemie*, vol. 5, 1829, p. 31.

² Minutoli. Bemerkung über die Anwendung der Traubenkerne zur Oelbereitung. *Journal für Technische und Ökonomische Chemie*, vol. 10, 1831, p. 352.

³ Oel aus Traubenskernen. *Dinger's Polytechnisches Journal*, vol. 148, 1858, p. 238.

⁴ Marre, F. L'huile des pépins de raisin. *Revue Générale de Chimie Pure et Appliquée*, vol. 14, 1911, p. 186.

⁵ Paris, G. I Vinaccioli. *Le Stazioni Sperimentali Agrarie Italiane*, vol. 44, 1911, fasc. 8-9, p. 669.

Grape-seed oil. *Pure Products*, vol. 8, 1912, p. 217.

EXAMINATION OF RAISIN SEEDS FOR COMMERCIAL PRODUCTS.

The successful and profitable utilization of raisin seeds will depend not only upon the preparation of the various products obtainable, but also upon the practical uses to which they can be put. The object of this paper is to show not only what products can be made from the seeds, but also to point out the various channels of trade into which they may go in order to serve as important practical commodities.

The first step in the process of examination was to make use of the sugary matter which adheres to the seeds as they come from the seeding machines (fig. 2). From this material a very desirable sirup

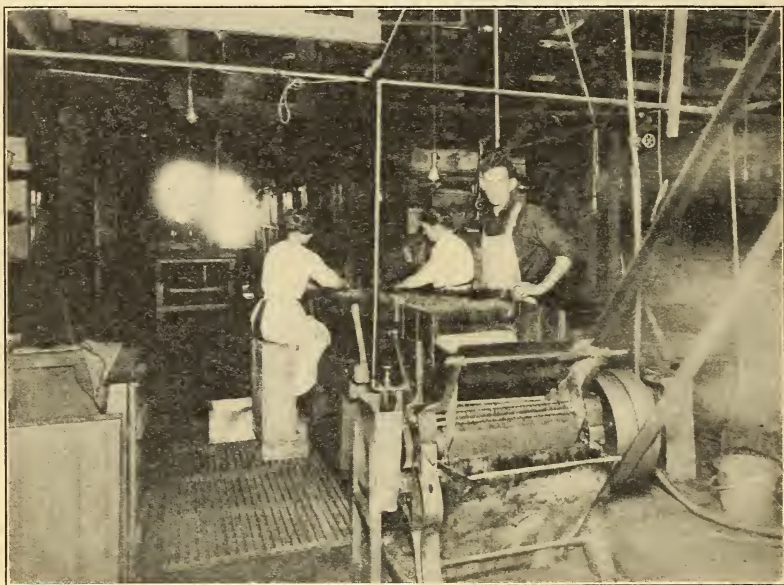


FIG. 2.—Raisin seeding machine in operation.

was prepared (fig. 3). The next step was to determine the quantity of fixed oil, since it is known that the seeds of practically all fruits contain fatty or fixed oil to a greater or less extent and that many such oils are important articles of commerce, entering into the manufacture of paints, varnishes, soaps, etc. (fig. 3). From the astringent taste of the seeds the presence of tannin was suspected, and since tannins are valuable articles of commerce a determination of the tannin content was next made (fig. 3). As a final product, after the extraction of the fixed oil and the tannin, the residue was analyzed for its possibilities as a stock food (fig. 3).

In the following pages each of the products mentioned is discussed separately in regard to methods of preparation, extraction, chemical

analysis, application in commerce, the approximate quantity available, and the probable value. The investigation of the seeds was taken up systematically, in order that every available constituent

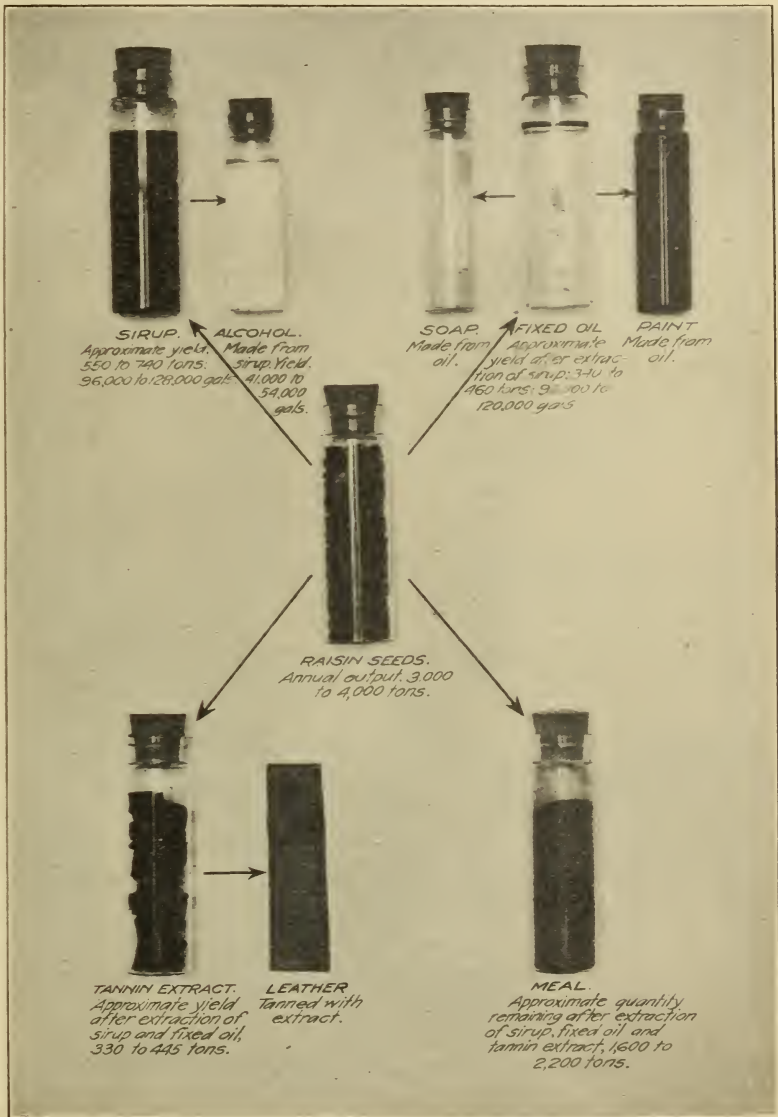


FIG. 3.—Commercial products from waste raisin seeds.

which is capable of being extracted practically might be given careful attention and that as many articles of commercial value as possible might be produced.

SIRUP.

PREPARATION.

As the initial step in the process of utilizing the waste raisin seeds, the material, which consisted of a sticky mass of seeds and pulp, was washed with cold water to remove the adhering pulp. The solution thus obtained was distinctly sweet and it was thought it might be of value in the preparation of a sirup. It was therefore concentrated on a water bath, and a yield of 18.5 per cent of an agreeable sweet sirup was obtained, which possessed the characteristic raisin taste. As the material was received directly from the seeding machines it represented, so far as the writer is aware, the average condition of raisin seeds with respect to the amount of adhering sugary matter, and these figures may therefore be taken as the average percentage of available sirup. It is probable, however, that seasonal conditions have a direct influence on the sugar content of the fruit and also that the effectiveness of the machines in removing the pulp would affect the quantity of sirup obtainable, since in some instances much more pulp is left adhering to the seeds than in others.

PHYSICAL PROPERTIES.

The sirup had a consistency about equal to that of strained honey and was reddish brown in color. The specific gravity at 22° C. was found to be 1.384.

CHEMICAL EXAMINATION.

SUGARS.

The percentage of sugars present was determined by volumetric assay with Fehling's solution. One gram of the sirup was found to reduce 122 cubic centimeters of Fehling's solution. The dextrose factor for Fehling's solution, previously ascertained, was 0.005. These results show, therefore, that 1 gram of the sirup contains 0.61 gram, or 61 per cent, of reducing sugars calculated as dextrose.

A weighed portion of the sirup was subsequently inverted by the addition of a few drops of hydrochloric acid and heating on a water bath for one-half hour. By this operation the cane sugar and perhaps other polysaccharids were inverted to monosaccharids. The total reducing sugars were then determined as glucose. The difference in the number of cubic centimeters of Fehling's solution required before and after inversion corresponds to the cane sugar in the sample. Two grams of the sirup after inversion required 12.4 cubic centimeters of Fehling's solution in excess of the amount required for dextrose. From the cane-sugar factor of Fehling's solution (0.00475) the total amount of cane sugar in the 2 grams of sirup was 0.0589 gram, which corresponds to 2.94 per cent of cane sugar.

ACIDS.

In connection with the intensely sweet taste of the sirup a slightly tart taste was noticeable, which was doubtless due to the presence of grape acids. The acidity was determined in terms of tartaric acid. Two grams of the sirup by titration with standard N/10 potassium-hydroxid solution required 2.85 cubic centimeters of alkali, which, from the tartaric-acid factor for decinormal alkali (0.007446), corresponds to 0.0212 gram of tartaric acid, or 1.06 per cent.

This analysis of the sirup indicates the composition only in a very general way as far as sugars and free acidity are concerned. Many factors may enter to vary the composition. The consistency of the sirup will have much to do with the percentage of sugars; the more the sirup is evaporated the higher will be the percentage of sugar, and vice versa.

PRODUCTION OF ALCOHOL.

As the sirup contains such a large quantity of fermentable sugar, the commercial production of alcohol from this by-product should be feasible. In order to determine the amount of alcohol capable of being fermented, 150 grams of the sirup were dissolved in about a quart of water, to which a teaspoonful of fresh yeast was added. The mixture was allowed to ferment for about 24 hours at a temperature of 30° C., or until the evolution of carbon dioxid ceased. After filtering the solution it was acidified with phosphoric acid to neutralize any volatile alkalis which may have been present. The solution was distilled over a direct flame until all of the alcohol was removed from the flask. After making alkaline with potassium-hydroxid solution to neutralize any volatile acids present and distilling, 90 cubic centimeters of alcohol were obtained. The specific gravity of the alcohol was 0.930 at 22° C., which corresponds to 42 per cent of absolute alcohol by weight. The total amount of dilute alcohol therefore contained 35.1 grams of absolute alcohol. Calculating from the amount of sirup used in the experiment, a total of 23.4 per cent of absolute alcohol can be obtained by fermentation of the sirup.

From these results it is estimated that the total amount of alcohol (calculated as absolute alcohol) capable of being manufactured from the sirup would approximate 130 to 170 tons. This quantity of absolute alcohol would represent about 140 to 184 tons of alcohol U. S. P. (190 proof), which corresponds to 41,176 to 54 117 gallons.

COMMERCIAL USES.

With its agreeable flavor and sweet fruity taste, the sirup from raisin seeds possesses qualities which should make it useful in the household and also in various commercial industries. For instance, in

the making of mincemeat, in which large quantities of raisins are ordinarily used, the sirup could be used to a certain extent at perhaps less expense, certainly with less labor, and still the peculiar and agreeable flavor of the raisins could be retained. For table use it would seem to be distinctly desirable, since the flavor and wholesomeness of the raisins are to a great extent retained. A prominent manufacturer of sirups for soda-fountain use has pronounced it to be a most excellent flavor for carbonated drinks, and it should find use in this direction.

The outlook, therefore, for creating a demand for this by-product is very promising.

AVAILABLE QUANTITY AND VALUE.

In view of its possible commercial uses, the question of the approximate quantity available and the value of the sirup is important. Since 3,000 to 4,000 tons of seeds are available annually from the seeded-raisin industry and since approximately 18.5 per cent of sirup is obtainable from this material, it follows that 555 to 740 tons could be manufactured yearly. This is the equivalent of 1,110,000 to 1,480,000 pounds, or, calculating from the specific gravity of the sirup, 96,522 to 128,696 gallons.

The value will, of course, depend largely upon the channels of trade into which it is directed. A conservative estimate, however, would place it at from \$30,000 to \$50,000 annually, provided a demand for the product is created in which its usefulness is assured, and it is not unreasonable to assume that some of the suggested uses will eventually build up a steady demand for this product.

FIXED OIL.

EXTRACTION AND PHYSICAL PROPERTIES.

After removing the sugary pulp, the seeds were screened, dried, and ground, and then extracted with ether in a continuous-extraction apparatus. A yield of about 14.5 per cent of a pale, golden-yellow oil was obtained, which possessed a slightly fatty odor with a bland, nutlike taste. The specific gravity at 24° C. was 0.9220 and the index of refraction at 25° C. was 1.4702.

CHEMICAL EXAMINATION.

FREE ACIDS.

The amount of free acids in the oil was ascertained by titrating a weighed quantity of the oil with alcoholic potassium hydroxid. One gram of the oil was found to require 1.25 milligrams of potassium hydroxid for neutralization, corresponding to 0.62 per cent of free acid calculated as oleic acid.

SAPONIFICATION VALUE.

As a measure of the glycerids of fatty acids, the saponification number (Koettstorfer number) was determined by heating a weighed quantity of the fixed oil with a definite volume of alcoholic potassium hydroxid and titrating back the excess of alkali with standard hydrochloric-acid solution. The saponification value, or the number of milligrams of potassium hydroxid required to saponify the fatty-acid glycerids in 1 gram of the oil, was found to be 188.

IODIN ABSORPTION.

The property of iodine absorption possessed by fixed oils is dependent upon the presence of unsaturated fatty acids or fatty-acid glycerids. It is a property of all unsaturated fatty acids to take up iodine by direct addition, the amount absorbed depending upon the nature of the unsaturated compounds or the number of double bonds they contain. Saturated fatty acids and their glycerids containing no double bonds do not possess this property. The iodine number is therefore an indication of the composition of a fixed oil as regards the content of unsaturated fatty acids and often determines the class of oils to which it belongs.

The iodine absorption of raisin-seed oil was determined in the usual manner, that is, by allowing iodine to react under the conditions directed ¹ with a definite quality of oil and titrating the excess by means of standard sodium-thiosulphate solution. The iodine absorption (or Hübl's) number was found to be 131.

VOLATILE ACIDS.

It has been stated that fixed oils consist largely of glycerids of fatty acids. The fatty acids in combination with glycerin may be either volatile or nonvolatile, the latter usually predominating. Fixed oils often contain in combination small quantities of some of the soluble volatile acids, such as butyric, valerianic, caproic, and caprylic, which decrease in solubility as well as in volatility in the order mentioned. The Reichert-Meissl number is a measure of the amount of volatile acids present in a fixed oil and is indicated by the number of cubic centimeters of decinormal alkali required to neutralize the volatile fatty acids obtained from 5 grams of fixed oil.

The determination of volatile acids was carried out in accordance with the method recommended by the Association of Official Agricultural Chemists ² and consisted essentially in saponifying a weighed portion of the oil in 95 per cent alcohol by means of sodium-hydroxid solution, then evaporating the alcohol, dissolving the soap in water,

¹ United States Pharmacopeia, 8th revision, p. 527.

² Official and provisional methods of analysis. Bulletin 107 (revised), Bureau of Chemistry, U. S. Dept. of Agriculture, 1910, p. 139.

acidifying, and distilling with steam. By titrating the distillate with standard alkali solution the volatile-acid equivalent of 5 grams of fixed oil, expressed in cubic centimeters of tenth-normal alkali solution, was readily ascertained. By this method the Reichert-Meissl number, or the amount of volatile acids in the oil, was found to be 0.64, which indicates that a very small percentage of the lower volatile acids is present.

SOLUBLE ACIDS.

The percentage of soluble acids was also determined according to the method prescribed by the Association of Official Agricultural Chemists¹ and consisted in liberating the fatty acids from a saponified weighed portion of oil by the addition of a definite amount of half-normal hydrochloric acid. After washing the liberated fatty acids several times with hot water, the aqueous solution was titrated with tenth-normal alkali. By means of the factor 0.0088 the weight of the soluble acids in the saponified oil was calculated as butyric acid. By this method it was found that 6.697 grams of raisin-seed oil contained 0.0264 gram of butyric acid, which corresponds to 0.394 per cent of soluble acids.

INSOLUBLE ACIDS.

The amount of insoluble fatty acids (Hehner value) was also determined by the method adopted by the Association of Official Agricultural Chemists.² The insoluble fatty acids remaining from the determination of the soluble acids were drained and dried. They were then transferred to a weighed dish and the filter paper through which the soluble acids had been filtered was washed with absolute alcohol and the flask which contained the insoluble acids was rinsed with absolute alcohol. The filtrate and washings were then added to the insoluble acids in the weighed dish. After drying in a desiccator, when the alcohol had evaporated and the weight of the acids had become constant, the weight of the insoluble fatty acids in the oil corresponded to a total of 94.4 per cent. Since the uses of an oil are largely dependent upon the nature of the insoluble acids which it contains in the form of glycerids and since so large a proportion of raisin-seed oil consists of insoluble acids, this subject will be discussed in detail later in this bulletin.

ACETYL VALUE.

As a measure of the hydroxylated glycerids in a fixed oil, the determination of the acetyl value is usually made. Acetic-acid anhydrid is employed to react with the hydroxy groups that may be contained in the fatty acids, the acetyl radical (C_2H_3O) replacing the hydrogen of the hydroxy (OH) group. The method used was again that

¹ Op. cit., p. 138.

² Op. cit., p. 139.

recommended by the Association of Official Agricultural Chemists.¹ After acetylation of the oil with acetic-acid anhydrid it was washed free from excess acid and dried. By saponifying a weighed portion of the acetylated oil, dissolving the soap in water, and decomposing the soap with a quantity of sulphuric acid equivalent to the amount of potash added, the free acids were liberated. The insoluble fatty acids separated in the form of a layer, while the soluble acid (acetic) which was taken up during acetylation remained in solution. After carefully washing the oily acids with boiling water, the aqueous acid solution was titrated with standard alkali and the amount of acetic acid determined.

The acetyl value of raisin-seed oil, after correcting for the soluble volatile acids as suggested by Lewkowitsch,² was found to be 16, which indicates that 16 milligrams of potassium hydroxid were required to neutralize the acetic acid obtained by the saponification of 1 gram of acetylated oil. This value is considerably lower than the results obtained for grape-seed oil recorded by Marre,³ which varied from 20.8 to 25.0.

UNSAPONIFIABLE MATTER.

Besides the glycerids of fatty acids, most fixed oils contain small quantities of unsaponifiable matter, which consists principally of an alcoholic substance, phytosterol, together with some coloring matter and compounds of a waxlike character. The amount of unsaponifiable matter sometimes varies in the different oils, depending upon the condition of the material as well as the methods of extraction. Although these constituents are of little practical value, a determination was made by saponifying a quantity of the oil with alcoholic potassium hydroxid and subsequently shaking out the aqueous solution of the soap with ether, and the oil was found to contain 0.78 per cent. The determination is useful chiefly for the detection of adulterations of vegetable oils with waxes, paraffin, or mineral oils.

DETAILED EXAMINATION OF THE INSOLUBLE ACIDS.

The insoluble acids, which comprise such a large proportion (94.4 per cent) of the constituents of raisin-seed oil, determine in a general way the usefulness of this oil. Insoluble acids are variable in character, some being solid at ordinary temperatures and others liquid. Oils with solid acids predominating are usually found useful in the manufacture of soaps, as, for instance, coconut and palm oils, which contain large quantities of such solid acids as stearic, palmitic, and myristic.

¹ Op. cit., p. 142.

² Lewkowitsch, J. *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. 1, 1909, p. 342.

³ Marre, F. *L'huile des pépins de raisin. Revue Générale de Chimie Pure et Appliquée*, vol. 14, 1911, p. 186.

The nature of the liquid acids of an oil also determines in many cases its practical application. Certain liquid acids are useful in soap making, while others possess drying properties, depending largely upon their constitution. It must be understood, however, that the free acids are not found to any great extent in a fixed oil, but are present as glycerids.

The insoluble acids of raisin-seed oil are both solid and liquid. Since the liquid acids are greatly in excess, the mixed acids when liberated from the oil are liquid.

MIXED ACIDS.

The insoluble acids separated from the oil after saponification by the addition of hydrochloric acid were obtained in the form of a golden-yellow liquid with practically no odor and with a bland, fatty taste becoming slightly bitter. The specific gravity at 24° C. was 0.8948, and the index of refraction at the same temperature was 1.4622. The acids began to congeal at 12.5° C. and were entirely solid at 11.5° C.

By titrating the oil with standard potassium hydroxid the neutralization value of the mixed acids was found to be 174.5. The iodine value, determined in the manner previously mentioned, was 137.

SEPARATION OF THE SOLID AND LIQUID ACIDS.

In order to separate the solid and liquid acids in the mixture, the lead-ether method was used. The effectiveness of this method depends upon the insolubility of the lead salts of the solid fatty acids in cold ether, the lead salts of the liquid acids being soluble. The method used for the preparation of the lead salts of fatty acids was that recommended by the Association of Official Agricultural Chemists under the test for peanut oil.¹ After saponifying about 5 grams of the oil with alcoholic potash, the soap mixture was neutralized with dilute acetic acid. The neutralized mixture was washed into a flask containing 25 cubic centimeters of water and 30 cubic centimeters of a 20 per cent solution of lead acetate. After boiling, the precipitated soap was cooled by immersing the flask in water and was agitated to cause the lead soap to stick to the sides of the flask. After decanting the water and excess of lead acetate and washing the adhering soap with water and 90 per cent alcohol, 50 cubic centimeters of ether were added and the mixture allowed to stand, after which it was heated for five minutes on a water bath with reflux condenser. The ether solution of the soap was then cooled in a refrigerator over night and the insoluble soap allowed to crystallize out.

¹ Official and provisional methods of analysis. Bulletin 107 (revised), Bureau of Chemistry, U. S. Dept. of Agriculture, 1910, p. 145.

To secure a separation of the solid fatty acids from the liquid acids, the method prescribed by the Association of Official Agricultural Chemists was again followed.¹ After filtering the lead-salt mixture, the insoluble lead soap on the filter was washed into a flask, decomposed with hydrochloric acid, and the mixture heated until the fatty acids melted. The flask was filled with hot water to bring the melted acids into the neck, and then cooled. After decanting the water, the acids were again washed in a similar manner. The solid acids were finally dissolved in hot absolute alcohol and the solution allowed to evaporate. After drying and weighing, the amount of solid acids in the raisin-seed oil was found to be 8.4 per cent.

The ether filtrate from the lead soap, which had been saved and which contained the lead salts of the liquid fatty acids of the oil, was placed in a separatory funnel and decomposed with 40 cubic centimeters of a 20 per cent solution of hydrochloric acid. The precipitated lead chlorid was separated from the ether solution and the latter washed until free from acid. The ether solution of the liquid fatty acids was evaporated in an atmosphere of carbon dioxid to prevent the oxidation of the acids. After evaporation of the ether, the amount of liquid fatty acids was found to be 84.7 per cent.

SOLID ACIDS.

The solid acids obtained by the above process appeared as a white, tallowlike, odorless, tasteless mass. The mixed solid acids after recrystallization melted at 57° to 58.5° C. By titrating a weighed portion of the solid acids with standard alcoholic potassium-hydroxid solution, 1 gram required 0.2163 gram of potassium hydroxid, which corresponds to a neutralization value of 216.3. Calculated from this neutralization value, the mean molecular weight of the solid acids is 259.

The neutralization value and the mean molecular weight of the mixed solid acids would seem to indicate the presence of palmitic and stearic acids, inasmuch as palmitic acid has theoretically a neutralization value of 219.1 and a molecular weight of 256, while stearic acid has a neutralization value of 187.5 and a molecular weight of 284. By comparing the theoretical figures with those actually obtained, it appears that palmitic acid is considerably in excess of stearic acid. This is further partially substantiated by the fact that the melting point of the mixed acids is much lower than that of pure stearic acid, which melts at 69° C., and is even lower than that of pure palmitic acid, which melts at 62° C. As the mixed acids were recrystallized only once, the presence of traces of impurities would perhaps account

¹ Op. cit., p. 142.

for the rather low melting point. Commercial stearic acid, which contains some impurities, is known to melt as low as 56°C .

Taking advantage of the difference in solubility of these two acids in alcohol and hydroalcoholic solutions, a precipitation method was applied with good success. A small quantity of the mixed solid acids was dissolved in alcohol to a clear solution. The alcoholic solution was diluted with a small quantity of water, which produced a flocculent precipitate. This fraction was separated and dried. Another equal quantity of water was added to the filtrate, which produced a second precipitate, and this was likewise separated and dried. The neutralization value of fraction 1 was determined in the usual manner and was found to be 197.1, while that of fraction 2 was 220.3. These values correspond very closely to stearic and palmitic acids, respectively.

In order to ascertain the approximate proportion of the two acids in the mixture, a calculation was made from the mean molecular weight of the mixed acids, according to the method suggested by Lewkowitsch,¹ which is as follows:

Let X = percentage of palmitic acid, and M_1 = molecular weight.

Y = percentage of stearic acid, and M_2 = molecular weight.

M = mean molecular weight obtained.

$$X + Y = 100.$$

$$\frac{M_1 X}{100} + \frac{M_2 Y}{100} = M.$$

Substituting the values of M_1 , M_2 , and M in the formula, the following equation is obtained:

$$\frac{256 X}{100} + \frac{284 Y}{100} = 259$$

Calculating the values of X and Y , the percentage of palmitic acid was found to be 89.3 and of stearic acid 10.7. A mixture of palmitic and stearic acids in the proportion of 90 to 10 actually gives a neutralization value of 216.77 and a mean molecular weight of 258.8; hence, the percentages found indicate very closely the proportion of these two acids in the mixed solid acids.

Since 8.4 per cent of the original oil consists of solid acids, there is therefore 7.5 per cent of palmitic acid and 0.9 per cent of stearic acid in the oil. Since the oil consists of the glycerids of the fatty acids, it was necessary to reduce these percentages to terms of the corresponding glycerids. The glycerid palmitin contains 95.29 per cent of palmitic acid, and the glycerid stearin contains 95.73 per cent of stearic acid; therefore, making the calculations from the percentages of the free acids, it is found that raisin-seed oil contains 7.87 per cent of palmitin and 0.94 per cent of stearin.

¹ Lewkowitsch, J. Chemical Technology and Analysis of Oils, Fats, and Waxes, vol. 1, 1909, p. 515.

LIQUID ACIDS.

The liquid acids of all fixed oils are usually unsaturated compounds with one or more double bonds in their molecular structure. Such unsaturated compounds possess the property of taking up oxygen, or, in other words, are readily oxidized, the compounds being changed into saturated hydroxylated compounds. In the case of the unsaturated fatty acids the resulting oxidation products are hydroxylated acids, which are easily characterized and identified.

When an oil consists largely of liquid fatty acids, as is the case with raisin-seed oil, the composition of these liquid acids or their glycerids is essentially important, since it largely determines the value of the oil in its application to the arts and manufactures. For use in the manufacture of paint, the presence of certain fatty acids is required; for soap-making purposes certain other acids are necessary; and for use as an edible oil still others must be present. The liquid acids obtained from raisin-seed oil were of a golden-yellow color and bland, lardlike odor. The taste was fatty and bland, with a bitter aftertaste. The specific gravity at 25° C. was 0.9020 and the refraction at 25° C. was 1.4640. The neutralization value of the liquid acids was 199.8 and the iodine absorption value 146.1.

Identification of the liquid acids.—In order to learn the composition of the mixed liquid acids obtained from raisin-seed oil, a small quantity of the acids was oxidized according to the method of Hazura and Grüssner¹ by means of a 1½ per cent solution of potassium permanganate. Of the fatty acids 5 grams were neutralized with 6 cubic centimeters of a 30 per cent solution of caustic potash. The resulting soap, after being dissolved in about 300 cubic centimeters of water, was oxidized with an equal volume of the potassiumpermanganate solution, added gradually and with constant agitation. Sufficient sulphurous acid was finally added to dissolve the manganese compounds and to impart an acid reaction. The precipitated hydroxylated acids were then extracted with ether in successive portions to remove the ether-soluble dihydroxystearic acid, if present. The ether solution was evaporated and the crystals recrystallized from alcohol. The crystals melted between 134° and 137° C. and were therefore dihydroxystearic acid, which when pure melts at 131.5° to 136.5° C. and is obtained by the oxidation of oleic acid.

The acids which were insoluble in ether were boiled successively with water, several deposits of crystals being obtained. The crystals melted at 158° to 159° C., which corresponds to the melting point of an isomer of sativic acid (tetrahydroxystearic acid) obtained as an

¹ Hazura, K., and Grüssner, A. Zur Kenntnis des Olivenöls. Monatshefte für Chemie, Bd. 9, 1888, p. 944.

oxidation product of linoleic acid. In addition to dihydroxystearic acid and tetrahydroxystearic acid a few crystals were obtained which melted at 207° C. and which were probably hexahydroxystearic acid or linusic acid, which when pure melts at 203° to 205° C. The presence of this oxidation product would seem to indicate that a trace of linolenic acid also exists in the liquid acids.

The liquid acids of raisin-seed oil apparently consist for the most part of oleic and linoleic acids, with a possible trace of linolenic acid. The neutralization value of 199.8 and the iodine absorption 146.1 of the liquid acids both point to the presence of oleic and linoleic acids, since the neutralization value of pure oleic acid is 198.9 and the iodine absorption 90.07, while linoleic acid possesses a neutralization value of 200.4 and an iodine absorption value of 181.4.

The mean molecular weight of the liquid acids, calculated from the neutralization value 199.8, was found to be 280.78, which further supports the view that the acids consist mainly of oleic and linoleic acids, which have a molecular weight of 282 and 280, respectively. Using the equation given under solid acids and calculating from the mean molecular weight (280.78) for the determination of the proportions of oleic and linoleic acids present in the mixed liquid acids, it was found that linoleic acid predominates, being present to the extent of 61 per cent, while the remaining 39 per cent corresponds to oleic acid.

These results were further confirmed by calculating the proportions of oleic and linoleic acids from the iodine value of the mixed acids, which was 146.1. The iodine value of oleic acid is 90.07 and of linoleic acid 181.42. Hence, letting X equal the percentage of oleic acid and Y the percentage of linoleic, the following equations are derived:

$$\begin{aligned} X + Y &= 100. \\ \frac{90.07 X}{100} + \frac{181.42 Y}{100} &= I \text{ (iodine absorption of mixed acids).} \end{aligned}$$

Substituting the value of I and finding the values of X and Y , the results indicate that 61.3 per cent is linoleic acid and 38.7 per cent is oleic acid.

It has been previously stated that 84.7 per cent of the original oil consists of liquid fatty acids. Assuming that the proportion of linoleic and oleic acids in the liquid acids is approximately 61 and 39 per cent, the original oil contains about 51.7 per cent of linoleic and 33 per cent of oleic acid.

From these percentages the amounts of the glycerids linolein and olein can be calculated. It is known that linolein contains 95.67 per cent of linoleic acid and olein contains 95.7 per cent of oleic acid. Hence, calculating by simple proportion, it is found that the oil consists approximately of 54 per cent of linolein and 34.48 per cent of olein.

Briefly summarizing the results obtained from the chemical examination of raisin-seed oil, the following composition is indicated:

	Per cent.
Linolein.....	54
Olein.....	34.48
Palmitin.....	7.87
Stearin.....	.94
Free acids (calculated as oleic acid).....	.62

The remainder of the oil consists of small amounts of volatile acids, soluble acids, and unsaponifiable matter, with possibly a trace of the glycerid of linolenic acid.

DRYING PROPERTY OF RAISIN-SEED OIL.

Since the fixed oil of raisin seeds contains constituents with drying properties, it was thought advisable to determine the actual drying value in order to compare it with some of the standard drying oils. The drying property of a fixed oil depends upon its power to absorb oxygen and it must necessarily contain constituents which are readily oxidizable. This property is also greatly influenced by the condition of the oil. In the raw condition, untreated in any way, oils usually possess the power of oxygen absorption to a much less degree and with much less rapidity than when subjected to certain treatments, such as boiling or heating with compounds rich in oxygen. Simple continued heating of an oil modifies this property of oxygen absorption, rendering the oil more powerful in this respect. The most common method, perhaps, of rendering oils more susceptible to the absorption of oxygen is treatment with the so-called "driers." Common among these are lead oxid (litharge), manganese dioxid, and a combination of manganese with rosin known as manganese rosinate.

In order to determine the drying property of raisin-seed oil, the crude raw oil was treated first by heating for 30 minutes at 200° to 210° C.; second, by heating for 15 minutes at 190° to 200° C. with lead oxid varying in quantity from one-half of 1 to 4 per cent; and, third, by heating for 15 minutes at 190° to 200° C. with manganese dioxid varying in quantity from 1 to 4 per cent. A sample of raw linseed oil, chosen for the purpose of comparison, was treated in the same manner.

As has been stated, the drying of oils is accompanied by the absorption of oxygen. These results, therefore, an increase in weight and the percentage of this increase determines the drying quality of the oil. Although some oils when exposed to the air gradually absorb oxygen and become dry, yet the less the quantity the more rapid the process, and in order to complete the experiments as rapidly as possible they were carried out in the following manner: Thin layers of the prepared oils, ranging in weight from 12 to 14 centigrams, were

spread evenly over small glass plates having an area of 25 square centimeters. The plates were then set aside in a place free from dust but with free access of air. They were carefully weighed from time to time and the percentage of increase computed. The weighings were conducted over a period covering the time required in each case for the maximum absorption, the period varying with the different samples and the different treatments. The results are given in Table I.

TABLE I.—*Oxygen absorption, or percentage of increase in weight, of films of raisin-seed and linseed oils when treated in various ways.*

Length of exposure.	Raw.		Heated.		Heated with PbO.								Heated with MnO ₂ .					
					One-half of 1 per cent.		1 per cent.		2 per cent.		4 per cent.		1 per cent.		2 per cent.		4 per cent.	
	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.	Raisin-seed oil.	Linseed oil.
Hours.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
5	1.7	2.29	(1)	(1)
6	0.24	0.23	5.1	7.8	5.7	9.3	2.8	9.8
22
23	6.76	11.6	8.4	13.3	8.4	12.8	7.6	12.0
24	(1)	(1)	.32	.47	(1)	(1)
29	8.8	13.7	8.78	13.0	8.2	12.0	(1)	(1)
48	(1)	(1)	.4	.47	8.67	13.2	8.8	13.7	8.2	13.2	7.3	12.2	(1)	(1)	.3	1.3	.47	9.9
72	(1)	(1)	.4	.47	9.12	13.2	8.8	13.5	8.1	13.0	7.3	11.9	0.23	0.94	.52	13.7	1.5	13.9
96	1.2	1.1	8.6	13.2	8.2	13.3	7.2	12.8	6.4	11.7	.63	3.6	.82	13.9	2.4	13.7
120	(1)	(1)	2.0	1.66	8.0	12.7	7.7	7.2	12.8	6.2	11.7	1.1	10.7	1.7	13.9	3.8	13.5
144	(1)	(1)
168	5.87	8.4	6.4	12.6	7.1	6.66	12.6	6.0	11.7	4.64	14.0	5.0	12.9	8.29	13.0
192	0.24	0.76	8.52	13.1	6.7	13.5	7.26	12.3	9.99	12.7
216	.4	3.3	10.6	14.1	6.1	5.9	11.6	5.4	11.4	8.5	13.3	8.83	11.2	9.92	12.1
240	.65	7.8	9.7	13.4	9.36	9.58	9.79
264	9.1	12.9	10.0	10.0	9.38
288	1.95	14.1	8.76	12.6	8.76	9.9	9.73	8.85
312	2.75	13.1
336	4.53	12.4	8.88	8.84	8.1
360	6.88	11.1	7.0	11.7
384	8.43	10.6
408	9.32	10.6
432
456
480	7.1	9.6

¹ No increase.

An analysis of the table shows that the raw oils absorbed oxygen very slowly, both oils beginning absorption at about the same time. The percentage of increase, however, was much more rapid from hour to hour in linseed oil than in the oil from raisin seeds. The latter attained its maximum absorption in 408 hours, a total of 9.32 per cent of oxygen being absorbed, while the linseed oil reached its limit in 288 hours, with a total oxygen absorption of 14.1 per cent. Both films were dry but gelatinous, the raisin-seed oil film being a trifle more sticky than that of the linseed oil.

The heated oils absorbed oxygen much more quickly than the raw oils. An increase in the weight was noted at the first weighing in 6

hours. The increase was steady and considerably more rapid than in the raw oils, the maximum in both oils being reached in 216 hours. The percentage of absorption was practically the same as in the raw oils, but the time of absorption was less in the raisin-seed oil, the heating, therefore, having the effect of hastening the drying.

The experiments show also that by heating the oils with lead oxid in quantities varying from one-half of 1 to 4 per cent, oxygen was absorbed with much greater rapidity than by the heated or raw oils. When heated with 1 and 2 per cent of lead oxid the films had practically become set in 6 hours, the absorption in raisin-seed oil amounting to 5.1 and 5.7 per cent, respectively, and in linseed oil to 7.8 and 9.3 per cent, respectively. Each of the oils treated with the varying quantities of lead oxid produced a film which at the end of 23 hours was dry, with only a slight stickiness. The maximum absorption in the case of raisin-seed oil was 8.1 to 9.12 per cent, and in linseed oil 12.2 to 13.7 per cent, which was about the same range. When heated with 4 per cent of lead oxid there was less total absorption in both oils than when heated with one-half of 1, 1, and 2 per cent. Apparently the oils heated with 1 and 2 per cent dried most rapidly in each case.

Manganese dioxid seemed to be much less efficient as a drier than the lead oxid, the length of time necessary to dry the films being in all cases considerably longer than when the oils were heated with lead oxid. Four per cent of manganese dioxid appeared to be the most favorable, the films of both oils drying more rapidly than when containing a less quantity. The maximum oxygen absorption of raisin-seed oil (9.99 per cent) was not reached until 192 hours, while linseed oil required only 72 hours, the total absorption being 13.9 per cent. Both the raisin-seed and linseed oils when heated with manganese dioxid produced films of about the same texture, drying to about the same degree of hardness as with the lead oxid.

In texture and tenacity the films in all the experiments bore a close resemblance, those of linseed oil being a trifle harder and a little less sticky than those of the raisin-seed oil. All were transparent and somewhat elastic and insoluble in ether. In all the experiments there seemed also to be a continual decrease in weight after the maximum absorption had been reached, the films becoming harder and less sticky.

COMPARISON OF RAISIN-SEED OIL WITH OTHER DRYING OILS.

Since only unsaturated fatty acids possess the property of taking up oxygen, this class of constituents is necessary to drying oils. Stearic acid is a saturated fatty acid and does not change on exposure to air. Oleic acid, on the other hand, contains two atoms of hydrogen less than stearic acid and is a common unsaturated fatty acid present

in many fixed oils. This acid, therefore, readily takes up oxygen. Saturated and unsaturated fatty acids are usually present in oils in combination with glycerin and are known as glycerids. These glycerids in the cases of some of the more common fats are known as olein, palmitin, and stearin.

Most drying oils contain constituents in common upon which the drying property depends. The most important of these constituents are the glycerids of linolenic and linoleic acids. These compounds absorb oxygen from the air very readily, forming a neutral compound known as linoxyn, which is the characteristic end product of all drying oils used in paints and varnishes. This property of oxygen absorption is sometimes called autoxidation. When exposed to the air, drying oils will oxidize, the time required for complete oxidation, or formation of linoxyn, depending upon the nature of the oil and the thickness of the layer exposed. This oxidizing property is favorably influenced when certain substances known as siccatives or driers are digested with the oil. Metallic oxids, such as lead oxid and manganese dioxid, and such salts as manganese and lead resinates are commonly employed siccatives. When oils are digested with any of these compounds the change of the unsaturated acids to linoxyn is considerably hastened, the siccatives, in a catalytic way, bringing about more rapid absorption. This is clearly shown in Table I.

Among the drying oils the most important are linseed, walnut, China-wood (tung), hempseed, sunflower, and poppy-seed oils. Those most commonly used in this country are linseed and China-wood oils. Linseed oil is the only one produced in the United States and occupies a foremost position as a paint oil. The liquid constituents of the drying oils mentioned contain either linolenic or linoleic acids, or isomerids of these acids, the acids occurring in combination with glycerin as glycerids. Oleic acid in the form of its glycerid, olein, is also a constant constituent of these oils. The linoleic and linolenic acids, however, are of chief concern from the standpoint of the usefulness of the oils in the manufacture of paints and varnishes.

The experiments recorded in Table I show that the maximum absorption of raisin-seed oil was 10.6 per cent, while that of linseed oil was 14.1 per cent. In both cases the figures were obtained from experiments conducted with the heated oils. When siccatives were employed the maximum absorption was not increased, but the operation was greatly hastened. This has also been shown by Lippert,¹ who experimented with lead oxid (litharge) and manganese resinate as driers. Linseed oil was heated to 150° C. for 15 minutes with

¹ Lippert, Walther. Zur Ermittlung der von trocknenden Oelen und Firnissen absorbirten Sauerstoffmenge. Zeitschrift für Angewandte Chemie, 1898, Heft 19, p. 431.

varying percentages of driers, the weight of the film being from 0.11 to 0.13 gram per 100 square centimeters. The following results were recorded:

TABLE II.—*Oxygen absorption of linseed oil when heated with manganese resinate and lead oxid.*

Heated with—	Gain in weight after—				Remarks.
	12 hours.	23 hours.	36 hours.	39 hours.	
Manganese resinate:	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
0.02 per cent.....	2.1	15.97	17 per cent in 55 hours.
0.06 per cent.....	4.89	15.48	15.69 per cent in 40 hours.
0.15 per cent.....	6.6	14.45	
0.2 per cent.....	6.46	14.02	
Lead oxid:					
0.34 per cent.....		8.5	11.1	
1.1 per cent.....		13.5	13.9	
2.5 per cent.....		12.7		
6.8 per cent.....		12.3		

The experiments with raisin-seed oil heated with lead oxid seem to bear out Lippert's conclusion that the use of driers beyond a certain percentage produces no appreciable difference in the absorptive power. In both raisin-seed and linseed oils (Table II) the use of more than 1 per cent of lead oxid indicated no increase in the absorptive power, the films being practically dry in 23 hours with almost the maximum of oxygen absorption. The use of more than 1 per cent of manganese dioxid also seems to have no distinctly favorable influence upon the drying of the films of either raisin-seed or linseed oil.

A number of fixed oils have been investigated by Weger¹ and Kuhl² with respect to their oxygen-absorption properties and for the sake of comparison with raisin-seed oil are here given:

TABLE III.—*Oxygen-absorption power of certain drying oils.*

Kind of oil.	According to Weger.		According to Kuhl.
	<i>Per cent.</i>	<i>Days.</i>	<i>Per cent.</i>
Linseed (foreign).....	18	3-7	17.5
China wood.....	14-16	3-8
Hempseed.....	13.5	4-4½	16.8
Poppy seed.....	13.4	6½	15.6
Sunflower.....	14.8
Walnut.....	19.6
Rapeseed.....	7.6	7
Olive.....	5.2	20
Peach kernel.....	10.5	29

These results show that the foreign linseed oil possesses a greater power of oxygen absorption than the American linseed oil, which was

¹ Weger, Max. Ueber die Sauerstoffaufnahme der Oele und Harze. Chemische Revue über die Fett- und Harz-Industrie, Jahrg. 5, 1898, p. 249.

² Kuhl, Dr. Die Firnisbildung der Oele. Pharmazeutische Zentralhalle, Jahrg. 51, 1910, p. 185.

used in the experiments previously discussed. It will be seen by carefully comparing raisin-seed oil with the oils mentioned that although it possesses drying properties somewhat lower than such standard oils as linseed, China wood, and walnut, yet it has good drying properties as compared with the other drying and semidrying oils.

RAISIN-SEED OIL AS A PAINT AND VARNISH OIL.

Taking into consideration the ready-drying property of raisin-seed oil, especially when treated with an ordinary drier such as lead oxid, it should be of value in the paint and varnish industries. Not only does the oil when treated with driers absorb oxygen rapidly, but it compares favorably with linseed oil in this respect. Granting, however, that linseed oil absorbs oxygen more rapidly, the nature of the films after drying is much the same, both being transparent and elastic. The linseed-oil film differs apparently only in being slightly less tacky.

In order to ascertain its value as a paint oil, a small quantity of the oil was submitted to a paint manufacturer for a practical test. Two kinds of paint were made up, one being an oxid red and the other a graphite. The oxid-red paint was made the same as with linseed oil. The vehicle of the paint was composed of 8 parts of raisin-seed oil, 1 part of spirits of turpentine, and 1 part of linseed oil and gum japan. The driers used in the japan were litharge and oxid of manganese. The base of the paint was red oxid.

The paint was found to be of the same usual body as linseed-oil paint and flowed nearly as well under the brush. It dried somewhat more slowly but produced a high-gloss finish. Red oxid was chosen because this particular oxid is known to be very destructive to linseed oil, the color quickly losing its brilliancy and the paint becoming dead and bluish purple.

After four months' exposure, from August to December, the paint prepared with raisin-seed oil had a fine film with a good finish and the oxid was still as brilliant as when applied, which was exactly contrary to the results obtained with the linseed-oil paint. In August a sample of the paint was applied to corrugated iron on the south side of a building exposed to the strongest sunlight in a smoky district adjacent to blast furnaces which continually gave off gases. In March, after seven months' exposure to these conditions, the paint still retained the true, perfect color of the oxid and the finish was intact. In the opinion of the manufacturers, this particular paint "stood up" very well, far better in fact than linseed-oil paint under the same conditions.

Raisin-seed oil is decidedly resistant to heat and declines to take on color even when heated to 500° F., whereas linseed oil darkens

considerably and takes on a greenish color. The somewhat slower drying properties of raisin-seed oil should not be especially detrimental to its usefulness, since this can doubtless be overcome by treatment of the raw oil with proper driers. The preliminary experiments have shown that it can be used in the manufacture of paint, and in the particular instance mentioned it acted better than linseed oil.

Since raisin-seed oil acts so well in the manufacture of paint it could unquestionably be used also with equal success in the manufacture of varnish, in which at present linseed and China-wood oils are used almost entirely.

As raisin-seed oil contains a large quantity of linoleic acid, together with some linolenic acid, it should also be capable of being oxidized to produce what are commonly known as oxidized or blown oils. These are drying or semidrying oils which have been artificially oxidized by heating in a current of air or oxygen and find extensive use in the various industries. It is probable that by the oxidation of raisin-seed oil there would result a substance similar to that formed from linseed oil (linoleum mass) which is used so extensively as a basis for making linoleums.

RAISIN-SEED OIL AS A SOAP-MAKING OIL.

For the purpose of testing the usefulness of raisin-seed oil in the manufacture of soap, a small quantity was saponified by the "cold process" with a calculated amount of strong sodium-hydroxid solution (about 30 per cent), the alkali being slightly in excess of the amount required to exactly saponify the given weight of oil. After standing 24 hours the excess of water was separated from the mass and the soap pressed into a cake and allowed to dry. A hard, compact soap resulted, which after several months still retained its white appearance, with only a trace of discoloration. Although this small quantity was made in a very crude way, yet, to all outward appearance at least, the sample, which produced a copious lather, showed that raisin-seed oil has some of the qualities of a soap oil.

This favorable preliminary test caused a desire to obtain the judgment of practical soap makers regarding the merits of the oil as a soap material. Accordingly, a sample of the fixed oil was submitted to a prominent soap manufacturer for a practical test. The soap chemist described the oil as being fair in color, but causing a somewhat deeper coloration upon saponification than some of the first-class soap oils. It was stated, however, that this could easily be removed by repeatedly salting out. It was also suggested that a process of refining or bleaching would remove the objectionable color and make it very suitable for use in the soap industry.

The soap was described as being about equal to olive-oil soap in color and as having a pleasant aromatic odor. Since the oil contains only a small percentage of palmitin and stearin, it was suggested that it could be used advantageously in the manufacture of toilet soaps in connection with tallow, palm oil, or coconut oil, which would have a tendency to produce a firmer soap with a higher melting point.

The fixed oils best adapted to the manufacture of fancy soaps are olive oil, palm oil, coconut oil, and almond oil. The latter, owing to its scarcity, is not used except for special purposes. Oils with high saponification value, such as coconut and palm oils, are used in connection with animal fats in order to increase their solubility and the lathering properties of the soap. Olive oil, which is much used in the manufacture of the finer grades of soaps, has a saponification value only slightly higher than raisin-seed oil.

It appears, therefore, from the tests conducted, that the oil of raisin seeds possesses qualities which should make it of considerable value in the soap industry.

AVAILABLE QUANTITY AND VALUE.

After removing the sugary matter for the preparation of the sirup there was found to be a reduction of about 20 per cent in the total weight of the seeds. Therefore, the weight of the seeds remaining would be from 2,400 to 3,200 tons. The average yield of oil being about 14.5 per cent, the total quantity of oil capable of being manufactured from this material would be approximately from 348 to 464 tons. Calculating from the specific gravity of the oil, this represents from 90,390 to 120,520 gallons available annually.

As a paint oil the value of the yearly production should approximate \$35,000 to \$50,000. In the manufacture of soap its value would perhaps be somewhat less.

TANNIN.

EXTRACTION.

In order to separate the tannin from the seeds after the extraction of the fixed oil, 1 kilogram of the residue was boiled out repeatedly with water and the aqueous extract evaporated. After evaporation there resulted 292 grams, or 2.92 per cent, of a semisolid extract, with a deep reddish brown color and a strong astringent taste. The moist extract contained 43.5 per cent of water; therefore, there would be 16.5 per cent of dry extract available. The dry extract was deep brownish red in color, breaking with a glassy fracture and having the odor of licorice.

ANALYSIS.

Upon analysis the dry extract was found to contain 28.38 per cent of tannins. Nontannins were present to the extent of 60.82 per cent.

The total amount of soluble solids was 89.2 per cent and of the insoluble material 10.8 per cent.

According to Trimble, tannins are divided into two general classes, known as the gallotannic-acid group and the oak-tannin group, the former including such tannins as are found in nutgall, chestnut bark, pomegranate bark, and sumac, while the latter group includes oak, mangrove, kino, canaigre, etc. The two groups are characterized by their behavior toward certain reagents, such as lime water, bromin water, and ferric chlorid. In order to determine the class to which raisin-seed tannin belongs, tests were made with these reagents. With lime water a reddish precipitate resulted, with bromin water a yellowish turbidity, and with ferric chlorid a green coloration was produced. These tests would place the extract in the oak-tannin group, since the same reactions are produced with oak tannins, while the gallotannic-acid group produces a blue precipitate with lime water, no reaction with bromin water, and a blue precipitate with ferric chlorid.

DYESTUFF.

In extracting the tannin considerable reddish coloring matter was also extracted. Although this coloring matter may be of no great importance as a dyestuff, its presence may add to the usefulness of the extract, since tanners often desire a coloring matter in connection with tanning extracts. Therefore, an examination was made as to its coloring properties.

As part of the coloring matter still remained in the residue after the extraction of the tannin, a small quantity of this residue was heated on a water bath with a 1 per cent solution of sodium hydroxid in successive portions. The deep purple-red solution was decanted and filtered in each case and neutralized with sulphuric acid. The dyestuff was precipitated in the form of a reddish brown flocculent mass, which was filtered, dried, and ground to a powder. In this manner about 18 per cent of a brownish red dyestuff was obtained, which was found to be readily soluble in dilute aqueous alkali to a purple-red color. In dilute acids it was less soluble, a yellowish coloration resulting. The powder was soluble in hot water to a brownish red solution. It was almost insoluble in ether, chloroform, and benzene, but was readily soluble in methyl alcohol to a red solution. It was somewhat less soluble in ethyl alcohol to a light brownish solution.

To test its properties as an indicator a small amount of the dye was dissolved by means of a few drops of tenth-normal sodium hydroxid and the purple-red solution diluted with water until the color was still distinguishable. Upon the addition of standard acid solution drop by drop, a sharp end reaction was noted, the change from purple red to yellow being readily seen. An aqueous solution,

when treated with mordant reagents, reacted by giving precipitates as follows:

Potassium bichromate.....	Brownish red.
Ferrous sulphate.....	Brownish red.
Stannous chlorid.....	Bright red.
Copper sulphate.....	Dirty brown.
Alum.....	Pale brownish red.
Zinc sulphate.....	Dark red.

After precipitating the dye from its alkaline solution by neutralizing with acid, the filtrate still possessed a reddish color, and after being evaporated down to about one-half its volume it was deep brown red in color. A small strip of cotton cloth was introduced into this solution and heat applied for about two hours, after which the cloth had taken on a deep-brown color. The dyed cloth was then mordanted with alum, after which it was dried and thoroughly washed with soap and water. After washing several times the cloth had a brownish red color, practically identical with that of the dyestuff.

Usually a variety of shades can be produced with a dye by means of different mordants. In order to ascertain the range of shades possible with the different metallic mordants, a crude dyeing experiment was carried out. The mordants chosen were chromium, iron, tin, copper, aluminum, and zinc. After immersing narrow strips of cotton cloth in the mordant solution for several hours they were transferred to neutral solutions of the coloring matter in question and heated for several hours, after which the strips were again immersed in the mordant and finally washed. The following shades were produced with the various mordants:

Potassium bichromate.....	Pale brownish violet.
Iron sulphate (ferrous sulphate).....	Grayish violet.
Tin chlorid (stannous chlorid).....	Light red.
Copper sulphate.....	Reddish violet.
Alum (aluminum-potassium sulphate).....	Brownish red.
Zinc sulphate.....	Light violet red.

It is very difficult to satisfactorily describe the shades produced, but distinct differences in color were apparent.

While the coloring matter or dyestuff may possess no direct value as a dyeing agent because of the cheaper and more available coal-tar dyes, it has been discussed principally for the reason that the tannin extract contains a considerable quantity of this substance and under the skillful manipulation of the tanner and the dyer it may be possible to produce tans of variable shades by the use of the different mordant solutions.

USE OF THE EXTRACT IN TANNING.

Partially to satisfy a desire to know whether the extract would be serviceable in the tanning of leather, a small quantity was submitted

to a commercial tanner for a practical test. The sample of leather tanned with the extract was fairly good in all general appearances. It was light reddish brown in color and was quite soft to the touch. It can not be said here whether this extract will compare favorably with some of the more common extracts, but from the test made and from the fact that it belongs to a class of tannins which are extensively used it does not seem unreasonable to suppose that it may find use in the leather industry, since a brisk and steady demand for tanning materials now exists.

AVAILABLE QUANTITY AND VALUE.

The quantity of seeds remaining after the removal of the pulp for the sirup and the extraction of the fixed oil would approximate 2,000 to 2,700 tons. This material is directly available for the preparation of tannin extract and as much as 16.5 per cent may be extracted from it. The total weight of dry tannin extract, therefore, which could be prepared is about 330 to 445 tons, or from 660,000 to 890,000 pounds annually. The value of the yearly output of this extract, roughly estimated, should be from \$19,000 to \$26,000.

MEAL.

The residue left after the extraction of the fixed oil and the tannin extract has been termed the meal and constitutes the greater portion of the by-product. It consists largely of protein, carbohydrates, and inorganic constituents, of which possibly the protein is of most importance. According to analysis the meal contains 1.94 per cent of nitrogen, which corresponds to 12.12 per cent of available protein. Other constituents have been determined as follows: Moisture 10.6 per cent, ash 2.4 per cent, crude fiber 43.2 per cent, nitrogen-free extract 30.5 per cent, and ether extract 1.2 per cent.

VALUE AS STOCK FOOD.

The utilization of the meal lies in its possibility as a stock food. The valuable constituents in stock foods are protein, carbohydrates, and mineral compounds. The protein comprises the nitrogen compounds present and is most essential for the formation of the nitrogen tissues and for the proper growth of the animal. Protein compounds are contained to a greater or less extent in practically all vegetable and grain foods which are used for stock feeding. The carbohydrates, in which are included crude fiber, starch, sugar, and gums, are also most essential as feeding stuffs and are present in all vegetable stock foods in varying proportions. The crude fiber or cellulose is present in large quantities in such feeding stuff as hay, straw, bran, and in the hulls of the various grains. Cellulose, while digested with difficulty, is considered to possess food value. The nitrogen-free extract

embraces starch, sugar, and some gums whose nutritive values are generally conceded. Practically all stock foods of value contain large percentages of nitrogen-free extractive which is readily digested and assimilated by the animal. Like the soluble carbohydrates, the ether extract or fat is an important fuel and fat-producing constituent of stock foods. Likewise, the mineral portion, or ash, of vegetable foods is also a necessary ingredient.

For the purpose of comparing the composition of raisin-seed meal with other stock foods, the following table has been compiled. Only four classes of stock foods are given, namely, hay, straw, grains, and hulls, as these most nearly correspond to the class of foods to which raisin-seed meal is most closely related. The figures represent the relative composition of the foods as given by Jordan.¹

TABLE IV.—*Comparison of raisin-seed meal with various feeding stuffs.*

Feed.	Moisture.	Ash.	Protein.	Fiber.	Nitrogen-free extract.	Ether extract.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Raisin-seed meal.....	10.6	2.4	12.1	43.2	30.5	1.2
Corn cobs.....	10.7	1.4	2.4	30.1	54.9	0.5
Oat hulls.....	7.3	6.7	3.3	29.7	52.1	1.0
Rice hulls.....	8.2	13.2	3.6	35.7	38.6	0.7
Buckwheat hulls.....	13.2	2.2	4.6	43.5	35.3	1.1
Cottonseed hulls.....	11.1	2.8	4.2	46.3	33.4	2.2
Peanut hulls.....	9.0	3.4	6.6	64.3	15.1	1.6
Oat straw.....	9.2	5.1	4.0	37.0	42.2	2.3
Rye straw.....	7.1	3.2	3.0	38.9	46.6	1.2
Wheat straw.....	9.6	4.2	3.4	38.1	43.4	1.3
Soy-bean straw.....	10.1	5.8	4.6	40.4	37.4	1.7
Timothy hay.....	13.2	4.4	5.9	29.0	45.0	2.5
Swamp hay.....	11.6	6.7	7.2	26.6	45.9	2.0
Alfalfa hay.....	8.4	7.4	14.3	25.0	42.7	2.2
Oats.....	11.0	3.0	11.8	9.5	59.7	5.0
Barley.....	10.9	2.4	12.4	2.7	69.8	1.8
Rye.....	11.6	1.9	10.6	1.7	72.5	1.7
Wheat.....	10.5	1.8	11.9	1.8	71.9	2.1
Corn.....	10.9	1.5	16.5	2.1	59.6	5.4
Buckwheat.....	12.6	2.0	10.0	8.7	64.5	2.2
Sunflower seeds.....	8.6	2.6	16.3	29.9	21.4	21.2
Cotton seeds.....	10.3	3.5	18.4	23.2	24.7	19.9

From a careful observation of the table it is evident that the moisture content of raisin-seed meal is much the same as in the various foods cited. In percentage of ash it corresponds more closely to the grains and is much the same as the hulls, with the exception of the rice and oat hulls. It is lower in ash content than the various hays and straws. In protein it greatly excels the hulls, hays, and straws, containing practically the same amount as the various grains. The high percentage of protein as compared with the various hays and straws should make the meal of considerable food value. The percentage of fiber is relatively high, while the nitrogen-free extract compares with that of the grain hulls mentioned. Since the meal contains

¹ Jordan, W. H. *The Feeding of Animals*, 1909, pp. 425-426.

about 30.5 per cent of nitrogen-free extractive it is fairly rich in soluble carbohydrates, which are of importance as a nutritive food. The ether extract or fat of the meal compares favorably with that of the hays, straws, and grain hulls.

Since raisin-seed meal contains considerable protein, together with a fairly high content of ash, soluble carbohydrates, and fat, it should possess useful feeding value. If mixed with other foods to supply the deficiency of some of its constituents, a well-balanced ration for the feeding of stock could be made and the meal thus profitably utilized. It should also be of some value as a constituent of chicken feed, since considerable protein is required in chicken rations.

AVAILABLE QUANTITY AND VALUE.

After the extraction of the tannin and the fixed oil from the raisin seeds there would remain about 1,600 to 2,200 tons of meal. The annual output of the meal, roughly estimated for its stock-feeding value, would be approximately from \$16,000 to \$23,000. Its feeding value would, however, necessarily have to be determined by actual feeding experiments.

SUMMARY.

In the preceding pages it has been shown that four important commodities, namely, sirup, fixed oil, tannin extract, and meal, are capable of being made from the large quantities of grape and raisin seeds which result from the seeding of raisins and the manufacture of wine and grape juice in this country.

Commercially, the manufacture of the sirup could be accomplished with comparative ease and readiness. Owing to the solubility of the sugars in water, the process of preparation resolves itself into simple extraction and concentration. Comparatively small quantities of water are necessary to completely dissolve the sugary matter from the seeds. The washing could possibly be most readily accomplished in large centrifuges, while the saturated solution requires only to be evaporated to produce the sirup. As the most convenient form of concentrating, vacuum pans would be the most efficient and expedient.

A clear, transparent sirup, with the characteristic delightful taste and flavor of the raisin, can be produced from the sticky seeds. Its uses are many and should justify its production from this waste material.

The fixed oil has been mentioned as found in considerable quantity in the seeds of raisins and also in the seeds of grapes which occur as by-products in the manufacture of wine and of grape juice. After washing off the sugary matter and drying and screening the

seeds, they need only to be ground for the production of the fixed oil. Two methods of extraction are feasible—by pressure and by solvents. Hot extraction by means of hydraulic presses would possibly yield the maximum of fixed oil. Cold pressure, having a tendency to incompletely extract the oil, would leave more fat in the press cake. Extraction by means of solvents such as benzene, carbon bisulphid, or low-boiling gasoline, or preferably, carbon tetrachlorid or trichlorethane, is practiced commercially because of the more complete exhaustion than by pressure, especially of materials with low oil content. The use of carbon tetrachlorid and trichlorethane has been recommended because of the noninflammable, nonexplosive properties of these solvents, both of which have comparatively low boiling points and are easily recovered. They are also capable of being used again for the same purpose.

The clear, amber-colored fixed oil, useful in paint and soap manufacture, and possibly in other industries, is capable of being produced in large quantities from the waste seeds. The important application of the oil in commerce, coupled with the large output available annually, should justify its production.

After the preparation of the sirup and the extraction of the oil from the seeds, the extraction of tannin has been recommended. The production of tannin extract is practicable only in the case of raisin seeds, since wine residues are probably largely depleted of their tannin content. The tannin, being soluble in water, can be extracted in a practical way by boiling the meal in large digestion vats, the solution being transferred to vacuum pans for concentration to a moist extract. If a dry extract is preferred it can be obtained by simply allowing the moist extract to dry in the air.

The large quantity of tannin extract which can be produced from raisin-seed meal and which is well adapted for the tanning of leather becomes the third important commercial product capable of being made from raisin seeds.

The final residue, the meal, seemingly already exhausted of all its constituents of value, still possesses useful qualities. The stock-feeding value of the meal has been discussed and a comparison made with several standard stock foods. While possibly it is not equal to some of the standard press cakes and meals on the market, yet on account of its high protein content its usefulness as part, at least, of a stock-feeding ration can hardly be denied.



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